APPLICATION OF MONOCARBOXYLIC SALT FOR PROTECTING LEAD AGAINST CORROSION

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Abstract

Currently, the hot topic in restoration and conservation of metals is the application of corrosion inhibitors intended for protection of lead. Our research aims in selection of suitable protection system which would be applicable for conservation of historical lead seals. Commonly, the seals are stored in archives together with documents to which the seal are attached. Vapour organic acids, acetic acid being a typical example, are the most aggressive pollutants in the archives environment considering corrosion of lead. The research was focused on determination of the inhibition efficiency after various manners of lead coupons pre-treatment (corroded and electrochemically cleaned). Sodium undecanoate was used as the inhibitor in concentration of 0.01 and 0.05 mol/l. The solution was applied by immersion for 24 h. Polarization resistance measurement and electrical resistance technique were used to evaluate inhibition efficiency in neutralised acetic acid environment. Artificially created corrosion products were analysed by X-ray diffraction analysis. Electrochemical cleaning of the surface provided high inhibition efficiency of the sodium undecanoate solution (0.05 mol/l). In general, the inhibitor was more efficient at higher concentration. It formed a layer of hydrophobic properties. Unfortunately, disadvantage of this layer is its low abrasion resistance.

Keywords: Corrosion inhibitor, lead seals, sodium undecanoate, polarization resistance

1. INTRODUCTION

Quite a lot of articles were already written about inhibition of lead corrosion with help of carboxylic acid. The common goal of the studies is to reduce corrosion of lead in environment of acetic acid with either solution [1] or suspension/dispersion [2] or melt of carboxylic acid. Acetic acid is the main product released to environment from degradation of organic materials such as cardboard packaging, which may be used for packaging in archives and deposits [1].

Current trend is to prefer preventive conservation before restorative action. That means to protect the object by controlling environment instead manipulating with object itself. One option of preventive conservation is a use of inhibitors. Inhibitor is "*a chemical substances that decrease the corrosion rate when present in the corrosion system at suitable concentration, without significantly changing the concentration of any other corrosion agen*t" [3]. Carboxylic acids, substances which we are using, are on boarder between inhibitors and substances which create conversion layers. Carboxylic acids (or their salts) react with lead or it´s corrosion products and create new layer on surface [4, 5]. But that isn´t conversion layer because according one of definitions conversion layer is „*inorganic crystalline insoluble layer or amorphous film*" [6].

In clean atmosphere the corrosion rate of lead is very low and on its surface thin layer of lead (II) oxide is created. In presence of atmospheric carbon dioxide, lead carbonate and basic lead carbonate are formed on the surface [7, 8]. In neutral atmosphere, corrosion rate is negligible under this layer of corrosion products. Corrosion rate increases in presence of vapour of acetic acid [1], which transforms lead carbonate to lead acetate, which is powder and fall off from surface.

The aim of this work was to determine inhibition efficiency of sodium undecanoate in environment of solution of neutralised acetic acid in dependency on previous surface treatment. Majority of previous works mostly examined inhibition efficiency on clean polished lead surface [1, 9]. It is very rare to encounter clean lead

surface while working with items in collections. The objects are usually covered with corrosion products. Therefore it is important for us to investigate an application of these inhibitors both on corroded surface and surface, from which of the corrosion products were removed. Considering the previous work [10] focused on electrochemical reduction of corrosion products, two approaches were followed: chemical cleaning in diluted sulfuric acid and electrochemical reduction of corrosion products in diluted sulfuric acid as well.

2.   EXPERIMENTAL

2.1.   Chemical

The corrosion environment was simulated by neutralised acetic acid solution. The original concentration of acetic acid solution was 0.05 mol / l [11], into which less than stechiometric amount of NaOH. Additional amount of NaOH solution (0.1 mol / l) was added afterwards in order to adjust pH to 7. Two dispersions of sodium undecanoate were prepared first with concentrations of 0.01 mol/l and 0.05 mol / l. Stechiometric amount of NaOH, needed for neutralization of undecanoate acid, was dissolved in 150 ml of distilled water. Undecanoate acid (99 %, Lach-Ner, s. r. o.) was gradually added into solution with constant stirring, until soft dispersion of salt was created. After that volume of dispersion was increased to 0.5 l.

2.2.   Lead soupons pre-treatment

Square lead samples (3 x 3 x 0.3 cm) were cut from pure lead (99.9 %) sheet. Lead surface was polished by using SiC emery paper while being cooled with water. Abrasiveness of last used sandpaper was P800, then was surface rinsed with ethanol and was dried off.

Artificial corrosion products were formed as follows. Clean ground coupons were submerged into solution of Na_2CO_3 with concentration of 1 mol / l for 48 h. In the middle of exposure, the solution was exchanged with fresh one. The samples were properly washed firstly with distilled water, then with ethanol and dried off.

Next set of samples was chemically cleaned after artificial corroding. Coupons were immersed into solution of H_2SO_4 with concentration of 0.5 mol / l for two hours.

Last set of coupons was submitted to electrochemical reduction using traditional three electrode arrangement. Saturated calomel electrode was used as a reference electrode, a platinum wire served as an anode and a lead coupon cathode was connected to minus pole of DC source. The electrochemical reduction was carried out in H_2SO_4 solution (0.5 mol / l), which was purged with nitrogen for an hour before and even during to the process for removing oxygen from the solution. Reduction itself was controlled potentiostatically. The lead working electrode was kept at -1.2 V with respect to saturated calomel electrode for two hours. This potential had been proved to be effective in reduction of corrosion product based on carbonates [12, 13].

The lead coupons were then submerged for 24 h into dispersion of sodium undecanoate. After extraction, they were rinsed with distilled water and dried off in room temperature.

2.3.   Measurement technique and measurement parameters

The polarization resistance technique was applied for assessing the efficiency of sodium undecanote in protection of lead against an action of acetic acid. The polarization resistance is universally proportional to corrosion rate. The measurement was carried out in a glass cell (30 ml) using a tree electrode arrangement. A platinum wire was used as a counter electrode and an activated titanium (mixed-metal oxide electrode) served as a reference electrode. Its potential was checked with saturated calomel electrode. A lead coupon (working electrode) was attached to the bottom of the cell that was filled with the electrolyte (exposed surface area was 1.33 cm^2). The polarization resistance was scanned by means of linear polarization every 10 min for 2 h in total. Each scan ran from -20 mV to 20 mV with respect to open-circuit potential with a rate of 1.66 mV/s.

The system was controlled by PC4 potenciostat (Gamry Instruments, Inc) .The inhibition efficiency of sodium undecanoate treatment was calculated from last value of polarization resistance (equation 1).

$$efficiency = \left[1 - \left(\frac{Rp_{surface\ without\ inhibitor}}{Rp_{surface\ with\ inhibitor}}\right)\right] * 100 \quad (\%) \tag{1}$$

Resistometric tests were carried out in a chamber (volume 10 l) exposing three electrical resistance probes at the same time. The relative humidity inside the chamber was kept approximately at 90 % with help of beaker filled with saturated solution of potassium hydrogen sulphate. Aggressiveness of atmosphere was controlled by beaker filled with 0.001 mol / l acetic acid. Resistometry is based on recording the electrical resistance of a thin track of a metal, the increase of which is related to the loss of metal track thickness. The first sensor was left free of artificial corrosion products. The second sensor was artificially corroded. The third sensor was artificially corroded and that inhibitor was applied afterwards. Another option of pre-treatment was the electrochemical cleaning of the sensors no. 2 and 3 after artificial corrosion products deposition. The corrosion depth of the sensors was scanned by means of ACD-03 logger (MetriCorr Corrosion Instruments).

XRD Analysis was done in order to identify the chemical compound of artificial corrosion products and the products resulting from submerging the specimens into the sodium undecanoate solution (PANalytical X'Pert PRO + High Score Plus).

3. RESULTS AND DISCUSION

3.1. Polarization resistance measurement

The stability of activated titanium electrode that served as the reference electrode during the polarization was checked by the SCE before and after measurement. Polarization resistances (R_p) were measured at least four times for each modification of surface treatment in environment of neutralized acetic acid with concentration of 0.05 mol / l. Final R_p values were statistically evaluated (**Table 1**). The lowest R_p values and so the highest corrosion rate were measured on samples which were chemically cleaned and no undecanoate was applied. The highest R_p values were measured on samples after electrolytic surface treatment and an application of the inhibitor with concentration of 0.05 mol / l. The magnitude of the standard deviation shows low reproducibility of the inhibitor application process.

Table 1 Mean final values of polarization resistance ($k\Omega \cdot cm^2$) in neutralised acetic acid environment (0.05 mol / l)

Surface condition	without $C_{11}H_{21}NaO_2$	standard deviation	with $C_{11}H_{21}NaO_2$ c = 0.01 mol / l	standard deviation	with $C_{11}H_{21}NaO_2$ c = 0.05 mol / l	standard deviation
ground	11.5	± 4	6.6	± 2.8	102.7	± 38.6
artificial corrosion products	4.2	± 1.7	18.4	± 11.4	596.6	± 506.2
chemical cleaning	0.5	± 0.2	67.3	± 32.8	3576.7	± 1122.3
electrochemical cleaning	1.3	± 0.3	7.7	± 1.2	10060.5	± 7101.9

Polarization resistance is getting stable to a constant value within 2 h of exposure. Surface treatment with sodium undecanoate solution results in by several orders of magnitude higher R_p values then the unprotected surfaces in all cases of surface treatments. The biggest difference is seen on chemically and electrochemically cleaned lead coupons, where unprotected surface has the lowest values of R_p and protected surface has the highest values.

The inhibition efficiency shown in **Figure 1** was calculated according to the equation (1) for both concentrations of inhibitor and for all modifications of surface treatment.
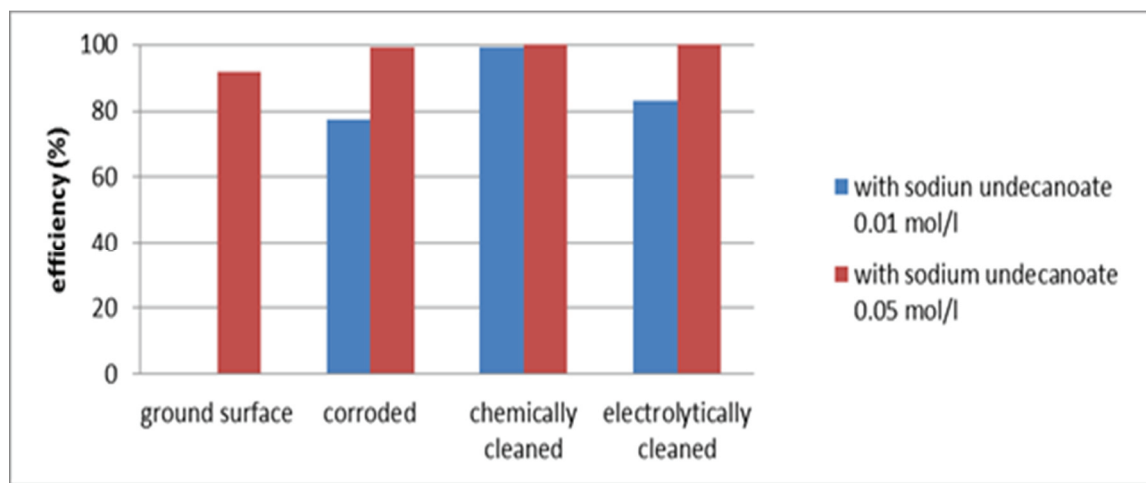

Figure 1 Inhibition efficiency of sodium undecanoate after application on pre-treated lead surface in neutralised acetic acid (0.05 mol / l)

3.2. Electrical resistance technique

Results obtained for two inhibiting solutions, sodium decanoate with concentration of 0.05 mol / l and sodium undecanoate with concentration of 0.01 mol / l, are available. It is assumed that both the compounds have similar protective action as it can be seen on experiments performed before. In humid atmosphere with fumes of acetic acid, the sensors with artificial corrosion products corroded faster and sensors with applied sodium decanoate and sodium undecanoate showed low corrosion rate (**Table 2**). Negative corrosion rate in several cases was probably caused by a decrease of resistivity of lead after grinding due to recrystallization or by corrosion attack of the reference part of the sensor.

Table 2 Corrosion rate of lead sensors in each period of exposition (µm/a)

| sensor	immersion in Na_2CO_3 solution (1 mol / l)		high relative humidity (≈ 90 %)		high relative humidity + acetic acid vapour	
	1st exp.	2nd exp.	1st exp.	2nd exp.	1st exp.	2nd exp.
ground			-0.4	0.7	-0.8	0.0
artificial corrosion products	221.2	441.9	3.3	80.8	4.8	82.5
artificial corrosion products + decanoate (0.05 mol / l)	1179.1	387.6	-1.3	-0.1	-1.3	-0.6
ground			26.4	23.2	11.9	14.2
artificial corrosion products	275	253.5	1.8	-0.1	26.7	8.9
artificial corrosion products + undecanoate (0.01 mol / l)	358.6	210.8	0.7	0.1	0.5	-0.2
ground			0.1	0.3	-0.1	-0.4
electrochemical cleaning	235.7	559.1	25.7	0.2	5.5	-0.8
electrochemical cleaning + undecanoate (0.01 mol / l)	318.5	974.1	-0.2	-0.4	-0.2	-0.8
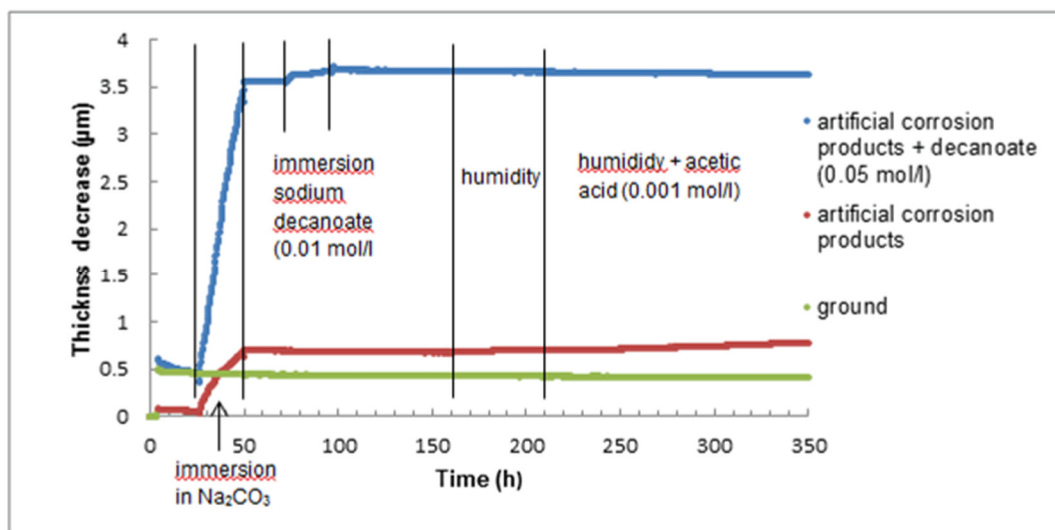
Figure 2 Record of electrical resistance measurement of three probes for 350 h

3.3. X ray diffraction analysis

Presence of corrosion products and a layer formed by submerging into inhibiting solutions was confirmed with XRD analysis. Overview of compounds found on samples surfaces is summarized in **Table 3**.

Table 3 X-ray diffraction analysis - semiquantitative composition of lead coupons surface

	-	litharge	cerussite	hydrocerussite	anglesite	lead caprate	-
surface condition	**Pb**	**PbO**	**PbCO$_3$**	**PbCO$_3 \cdot$Pb(OH)$_2$**	**PbSO$_4$**	**C$_{20}$H$_{38}$PbO$_4$**	**NaPb$_2$(CO$_3$)$_2$OH**
ground							
ground + undecanoate (0.01 mol / l)	4					3	
ground + undecanoate (0.05 mol / l)	4					4	
artificial corrosion products	3			2			4
artificial corrosion products + undecanoate (0.01 mol/l)	3	1	1		2	4	
artificial corrosion products + undecanoate (0.05 mol/l)	4	2		1		3	2
chemical cleaning	2	1			4		
chemical cleaning + undecanoate (0.01 mol / l)	3	1	1		2	3	
chemical cleaning + undecanoate (0.05 mol / l).	2				1	4	
electrochemical cleaning	4				1		
electrochemical cleaning + undecanoate (0.01 mol / l)	3	1		trace		3	
electrochemical cleaning + undecanoate (0.05 mol / l)	2	1				4	

1	**2**	**3**	**4**	
less than 5 %	5-25 %	20-40 %	more than 40 %	

4.   CONCLUSION

Inhibition efficiency of sodium undecanoate (0.01 a 0.05 mol / l) on lead coupons with various surface treatments was studied. High inhibition efficiency was observed for all modifications of surface treatments. The highest efficiency was observed after application of inhibitor with concentration of 0.05 mol / l. With higher concentration the layer, which is densely covered with flake crystals, is created. This layer is an efficient barrier against acetic acid solution. The highest inhibition efficiency was observed for electrochemically cleaned surface and the lower on clean ground surface. From the conservation/restauration point of view, the important finding is that extensive efficiency is provided by application of the inhibitor even on corroded surface. Unwanted side-effect is a slight change of overall colourfulness. Original dark grey becomes a little brighter. Cured item also has dim wax appearance. Direct measurement of lead corrosion rate by means of the electrical resistance technique proved that decanoate and undecanoate layer effectively protects lead against further corrosion in environment with increased relative humidity and acetic acid vapour. On the other hand, the newly formed layer is soft and it has low abrasion resistance. Dispersion preparation of sodium undecanoate is fairly tedious (stirring up to 24 h) to prepare solutions of undecanoate acid in ethanol would be easier because of better solubility. Therefore future works will deal with usage of ethanolic solutions

ACKNOWLEDGEMENTS

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